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**(56) Reference**

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#### **(57) Claim(s)**

**Claim 1** It is the bleaching agent composition protracted without containing an oxidizing bleach and an enzyme grain, and not involving intimate contact with an enzyme grain and an oxidizing bleach, either, but the stability of an enzyme spoiling fusibility unfairly, An oxidizing bleach chosen from a group which comprises an alkaline metal perboric acid salt, alkaline metal percarbonate, hydrogen peroxide adducts, and these mixtures, A bleaching constituent in which a hydrase enzyme grain which comprises a hydrase enzyme core with water-soluble alkali metal silicate coating which carries out the husk of the enzyme core substantially is comprised, and said coating contains a protecting agent which is a transition metal.

**Claim 2** The bleaching constituent according to claim 1 in which said oxidizer is sodium percarbonate.

**Claim 3** The bleaching constituent according to claim 1 chosen from a group to which said hydrase changes from protease, lipase, amylase, cellulase, and these mixtures.

**Claim 4** The bleaching constituent according to claim 3 in which said hydrase is protease.

**Claim 5** The bleaching constituent according to claim 1 in which said protecting agent comprises transition metal salt.

**Claim 6** The bleaching constituent according to claim 5 in which said transition metal salt is chosen from copper, nickel, iron, cobalt salt, and a group that comprises these mixtures.

**Claim 7** The bleaching constituent according to claim 1 in which said coating contains alkali metal carbonate further.

**Claim 8** The stability of an enzyme is strengthened in spite of a mothball under existence of an oxidizing bleach, It is a constituent of a dry granular oxidizing bleach and an enzyme in which the fusibility of an enzyme in inside of an aquosity medium is improved, a) An oxidizing bleach chosen from a group which comprises an alkaline metal perboric acid salt, alkaline metal percarbonate, hydrogen peroxide adducts, and these mixtures, hydrase by which the husk was substantially carried out thoroughly with an alkali metal silicate containing b transition metal, and \*\*\*\*\*\*, a bleaching constituent of a place.

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#### **Detailed Description of the Invention**

##### **Field of the Invention**

This invention relates to a cloth bleach for home use, more specifically uses an oxidizing bleach, especially an organic peroxy acid bleach as base resin, and relates to the dry bleaching constituent containing an enzyme. An enzyme exists as various grain coated in order to strengthen the stability in a bleaching constituent. Coating of an enzyme contains one sort or the active agent beyond it which protects an enzyme from degradation by a bleaching constituent.

##### **Background of the Invention**

The bleaching constituent is used at the home for bleaching of cloth, and wash for years. Since it is cheap and validity is high, and manufacture is easy and stable, the liquefied bleach based on a hypochlorite compound is used widely. However, new requirements go also into bleaching art by the appearance of modernistic synthetic dye, and use of a modernistic automatic washing

machine, and the necessity for the bleaching constituent of a different type is produced. In order to fulfill this necessity, and in order to develop the use of a bleach for home use widely, a bleach system different in recent years is introduced.

It is the dry bleaching constituent based on the peroxy acid compound that he is interested especially in recent years. A peroxy-acid compound is a chemical functional group. For drawings please refer to the original document.

It has high oxidation capacity by one \*\* or existence beyond it.

It is desirable similarly to prepare one sort or the enzyme beyond it for the purpose of dirt removal in addition to an activity oxidizer. By cleaving to the monomer or oligomer of low molecular weight which dissolves the dirt residue of the amount of Polymer Division in a wash medium easily, an enzyme degrades dirt of a certain kind and silverfish, and has the capability to promote removal or to transform a substrate to other refining things. An enzyme has an advantage of substrate specificity, i.e., an enzyme attacks only a unique combination and it does not have chemical influence on the substance which should usually be washed. \*\* -- the example of an enzyme **like** is an enzyme which can hydrolyze dirt, and is chosen from the enzyme group classified according to International union OBU biochemistry as "hydrase." Protease, amylase, lipase, and cellulase are classified into hydrase.

\*\*\*\* in which an enzyme denaturalizes easily by a harsh environment (molecular structure is changed) -- it is sensitive protein and a certain change can repeal an enzyme. If a strong acid voltinism bleach like organic acid peroxide has an oxidizing bleaching constituent of a certain concentration in the warm damp environment especially, it is harmful to the stability of an enzyme.

Various methods for stabilizing an enzyme and bringing about a good mixture with an enzyme, a detergent, or a bleach are proposed. an enzyme is variously looked like **carriers, such as clay, starch, and amine-ized polysaccharide**, , and they adhere to it, and it agglutinates a detergent carrier -- even having -- it is. Extrusion of the enzyme is granulated and carried out, and a husk is carried out to a film, and it can give a coloring-ized agent. In order to strengthen the stability of an enzyme, the trial which mixes an enzyme with protein, lowers the relative humidity of storage environment, divides a bleach into separate grain, or adds a reducing agent and a buffer for pH is made. However, especially the instability of the enzyme in a peroxy acid bleaching constituent is still continuing bringing about difficulty in the mothball of the peroxy bleaching constituent in which the bleach is densely mixed with the enzyme.

### **Summary of the Invention**

This invention relates to an enzyme content oxidizing bleaching constituent, especially the bleaching constituent based on organic 2 peroxy acid (JIPERU acid). More concretely, while this constituent supports the fusibility of an enzyme, it brings about the stability of an enzyme during the mothball under existence of an oxidizer.

An improvement constituent is prepared by coating or encapsulating an enzyme with the material which brings about sufficient fusibility, when an enzyme is effectively made into a tolerance \*\*\*\* thing to degradation in a bleaching constituent and it puts in an aquosity medium which is seen during wash. Especially an alkaline material works as a protecting agent, and before it contacts an enzyme and denatures an oxidizer, it is carbonated. \*\* -- the examples of a protecting agent **like** are a sodium silicate and sodium carbonate.

These both block the erosion to the enzyme by an oxidizer physically, and carbonate an oxidizer chemically.

What forbids radical chain oxidation of anti-oxidants, for example, BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), etc., such as a reducing agent, for example, sodium sulfite, and sodium subsulfite, again is contained in activity protection. A transition metal especially iron, cobalt, nickel, and copper work as a catalyst which brings destruction of an oxidizer forward, therefore protect an enzyme. These active oxygen protecting agents can be used with a carrier and the water-soluble polymer which commits fusibility as a dispersing agent or carriers for strength and a protecting agent although an enzyme is not especially protected by itself.

A standard bleaching constituent additive agent, for example, a builder, an extender, a buffer, a brightening agent, an aromatic, etc. can be added to individual enzyme grain and an oxidizing bleach, and can be included in an enzyme content oxidizing bleaching constituent.

Therefore, the purpose of this invention is to provide the enzyme protected from denaturation in the constituent containing an oxidizing bleach.

Other purposes of this invention are to provide the coated enzyme which is fusibility in an aquosity medium.

Other purposes of this invention are to provide the oxidizer bleaching constituent containing the enzyme in which the stability under preservation was enhanced.

The purpose of further others of this invention is to bring about the enzyme stable in the enzyme content peroxy-acid bleaching constituent.

#### **A concrete indication of an invention**

Unless it refuses in particular by the following, all the percentage, a ratio, or a part is based on weight.

**Enzyme** An enzyme is a publicly known additive to the ordinary constituent containing especially a detergent and a bleach, and by eroding dirt and silverfish, it works so that the cleaning effect of a detergent may be improved. The enzyme is sold in the form of the grain and the round or needlelike small aggregate.

The section of the grain (prill) of an enzyme is shown in the microphotograph of Fig. 1. When such a grain was added in a traditional dry detergent, it was tended to separate this enzyme from a detergent mixture. Granulating an enzyme as this difficult solution, i.e., make an enzyme adhere to carriers, such as starch or clay (granulation) or carrying out the spray of the enzyme directly on a solid detergent composition were performed. Such art was suitable about the comparatively mild dry detergent composition known in the past. However, it is not admitted that this granulation art is suitable to protect an enzyme from degradation by a more powerful new oxidizing bleaching constituent.

The enzyme which can hydrolyze a substrate, for example, dirt, is used for a usually mild bleaching constituent. The name received by the International union OBU biochemistry of these enzymes is hydrase. In hydrase, not limitation but protease (a protein system substrate is digested), Amylase (it is known also as carbohydrase and carbohydrate is digested), lipase (it is known also as esterase and a fat is digested), cellulase (cellulose type polysaccharide is digested), and these mixtures are contained.

Protease, especially alkaline protease are preferred to use by this invention. Since alkaline protease makes fusibility more the blood which especially hydrolyzes a protein substrate and becomes a problem, and herbal dirt, it is useful for especially a wash use.

Commercial alkaline protease. It is led by various races of bacteria (*Bacillus subtilis*). These protease is known also as the subdust gin (*subtilisins*) again. For the un-restrictive example of this, brand name Esperase\*\*, Savinase\*\*, and -- as Alcalase\*\* -- Novo industry A/S (Denmark.) protease and brand name Maxatase\*\* and Maxacal\*\* which can be obtained from Bug Suva Held -- Gist BUROKADESUN.V (the Netherlands.) There are a thing currently sold from Delft and a thing which is sold from Miles Laboratories (State Elkhart of Indiana), and is by brand name Milezyme\*\* APL. The mixture of an enzyme is also included in this invention. Also refer to US,4,511,490,B (SUTANISU Lossky etc.).

Commercial protease is supplied as a grain (prill), a granular material, or a ground enzyme. Stabilizer, for example, triethanolamine, clay, or starch can be included in these enzymes. In addition to protease, other enzymes can also be replaced with, and it can be used for this constituent. Lipase and amylase can find out a use to this constituent. Lipase is written in three columns of 15-55 lines of US,3,950,277,B. The description is used here. To suitable amylase, Rapidase\*\* (from SOSHIETE RAPIDAZE of France), There are Maxamyl\*\* (from Gist BUROKADESUN.V), Termamyl\*\* (from Novo industry A/S), and Milezyme\*\* DAL (from Miles Laboratories). Although cellulase is also mixed, it is desirable, and the US,4,479,881,B (Thailand), No. 4,443,355 (MURATA etc.), No. 4,435,307 (BABESU guard etc.), and No. 3,983,002 (OYA etc.) description is used.

A suitable enzyme level to use it by this invention is from about 0.1% from 0.4% to 2% most suitably 3% in 0.25% 10% based on the enzyme which is not coated.

**Oxidizing bleach** An enzyme tends to receive degradation by heat, humidity, and chemical action. If especially an enzyme contacts a strong oxidizer, it will denaturalize quickly. Generally a Prior art (granulation), for example, granulation, is not enough within a strong acid voltinism constituent which is based on a dry hypochlorite and a peroxy acid bleach to protect an enzyme. Moreover, the compound which generates hydrogen peroxide within an aquosity medium tends to have an operation harmful to the enzyme under preservation. There are an alkaline metal perboric acid salt (sodium perborate monohydrate or four hydrates), percarbonate (sodium percarbonate), and various hydrogen peroxide adducts in such a compound.

an oxidizing bleach -- general -- the inside of an aquosity medium -- about 0.1 to 50 ppm A.O.

(active oxygen) -- more generally about 0.1 to 30 ppm A.O. is given. A. The analysis of O. and a description are looked at by a "par acid and peroxide oxy day SHONZU" oxidation and pp 213-258 (1968) (Dr. S N Lewis). This description is used here.

An organic JI peroxy acid is a good oxidizer, and is known for the industry as a useful bleach.

An organic interesting JI peroxy acid may be compounded from much long chain diacid.

US,4,337,213,B (June 29, 1982, MARINOUSUKI, etc.) has indicated manufacture of the peroxy acid by making selected acid react to H<sub>2</sub>O under existence of H<sub>2</sub>SO<sub>4</sub>.

An organic JI peroxy acid has the following general structure.

For drawings please refer to the original document.

here -- R -- 4-20 carbon atom -- they are the straight chain alkyls from 6 to 12 more suitably. Especially a suitable thing is diperoxydodecane JIOIKKU acid (DPDDA). -- **here** -- R -- (CH<sub>2</sub>)<sub>10</sub>

And JIPERU azelaic acid (DPAA) -- **here** -- R -- , (OH<sub>2</sub>) -- it is .

It is for the detergent bleach containing peroxy acid also containing the exothermic depressant generally, and this protecting a peroxy acid bleach from febrile degradation by controlling the quantity of the existing water. A typical exothermic depressant is hydrated salt, for example, a MgSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> mixture. combining peroxy acid and an exothermic depressant in a granule --

\*\* -- making the stability of the enzyme which exists in a constituent increase is found out by adjusting the water content of a granule **like** carefully. Refer to U.S. Serial Number 899,461 under simultaneous pendency. The oxidizers of useful others are sodium perborate monohydrate and four hydrates, and sodium percarbonate in this invention.

Other additive components The additive component determined by the use of a constituent and preservation may be added by the bleach-enzyme constituent of this invention. The bleaching constituent is indicated by the simultaneous pendency U.S. application No. (August 12, 1986 application) 899,461.

The organic dicarboxylic acid of general formula HOOC-R'-COOH (R' is the carbon atoms from 1 to 10 here, and adipic acid is R'=(CH<sub>2</sub>)<sub>4</sub>, for example) is an additive agent desirable to a detergent bleaching constituent. \*\* -- organic acid **like** has the work which will dilute a JI peroxy acid (supposing it exists), and when using bleaching output, it helps the pH adjustment of wash water.

a JI peroxy acid -- an exothermic depressant -- and when it exists with a granular form with organic acid, especially the thing for which the physical integrity of grain is maintained is arbitrarily desirable by using a cementitious material. Such a material has the work which prevents a bleach's becoming powder during conveyance and handling, or being divided. Especially, the polymer acid which is not carbonated is interesting, and if this is used, per diperoxyacid in a detergent bleaching agent composition, an unpleasant smell of a thing can be decreased substantially or it can remove it.

Since the opposite operation of the fluorescence white agent (FWA) is carried out at yellowing of cotton and synthetic transition, it is an ingredient desirable although included in a bleaching constituent. FWA is absorbed by cloth in wash and (or) a bleaching process. FWA absorbs ultraviolet rays and functions by pouring this and making light emit as visible light of the blue wavelength range generally. The light of this result produces the glossy whitening effect, and carries out the operation which negates yellowing or the muddiness of cloth which this bleached. Such FWA can be commercially obtained with the trade name of "Tinopal" from Ciba-Geigy Corporation (Switzerland, BEZERU). Same FWA is indicated by the U.S. Pat. No. 3,393,153 item (gin MARA etc.). This description is used here.

In order to give protection of FWA -- an alkaline diluent (it protects from oxidation), and a cementitious material -- and it is arbitrarily mixable with bulking material, for example, Na<sub>2</sub>SO<sub>4</sub>, and a coloring matter. Subsequently, a mixture is compressed, particles (particle) are made and this is mixed with a bleaching constituent. The FWA particle can constitute about 0.5 to 10% of bleaching constituents (weight).

Generally the aromatic which gives a pleasant scent to a bleaching constituent is contained. Whether since an aromatic tends to receive oxidation by a bleach, it is encapsulated with polymer materials, such as polyvinyl alcohol, starch, or sugar is made to absorb an aromatic, and it may be protected by whether this is fabricated in a bead. Since these aromatic bead is fusibility at water, when a bleaching constituent is melted in water, an aromatic is released, but

the aromatic is protected from oxidation by a bleach during preservation. An aromatic is used also for giving a \*\*\*\* scent to the upper space of the container into which the bleach is put again. For example, refer to US,4,858,758,B (Mitchell etc.). A buffer, a builder, and (or) a bulking agent may also be made to exist in a bleaching constituent. Boric acid and (or) the sodium borate are suitable to carry out **of a constituent pH \*\*\*\*\***. Sodium carbonate, sodium bicarbonate, and other alkaline buffers are one of other buffers. A builder has organic builders, such as a sodium silicate and potassium, sodium phosphate, sodium tripolyphosphate, sodium tetrapolyphosphate, aluminosilicate (ZEORATO), and sodium sulfo succinate. A bulking agent can also be included. The most suitable bulking agent is sodium sulfate. A buffer and a bulking agent are granular and are added so that the whole constituent may turn into a drying constituent which carries out a dry flow. . 5 to 90% (weight) of range of a constituent may be sufficient as a buffer, and an another side builder and (or) a bulking agent are also 90% of ranges, and obtain them from about 5%. Coated enzyme The coated enzyme is prepared whether an enzyme is substantially coated with the material which permits sufficient fusibility thoroughly, and by encapsulating, when an enzyme is made into a tolerance \*\*\*\* thing at oxidation of a bleach and it puts into an aquosity medium. Various categories are among the active agents which protect the enzyme contained in coating. That is, they are alkalinity or neutral material, a reducing agent, an anti-oxidant, and a transition metal. These each may be used with other active agents of a category which is the same or is different. In a suitable embodiment, a reducing agent, an anti-oxidant, and (or) a transition metal are especially contained in coating which consists of an alkali metal silicate and (or) alkali metal carbonate in superior.

The most suitable coating also serves as a chemical barrier by neutralizing positively the oxidizer which a physical barrier is made to the attack by an oxidizer, and can be eliminated. the base (alkali) nature material exceeding pH about 11 -- more -- suitable -- the alkali metal silicate of pH 12 to 14 especially a sodium silicate, and \*\* -- the mixture with a silicate, alkali metal carbonate or bicarbonate, especially sodium carbonate brings about such suitable coating. ~~like~~ since the mixture with a silicate, this and carbonate, or bicarbonate forms a uniform vitrified matrix when the aquosity dispersion liquid are applied to the core of an enzyme -- especially -- \*\* -- it seems that it is better. this -- coating -- an effect -- oh, the necessity for the carrier material to close is abolished -- I will come out. The addition of alkali metal carbonate or bicarbonate can improve the fusibility of enzyme coating. \*\* -- the level in carbonate ~~like~~ or the silicate of bicarbonate can be adjusted so that the desired stability / soluble feature may be realized. pH of a salt or its mixture is measured as 10% solution of the salt.

There are some which were combined with one sort or the active agent beyond it which reacts chemically so that the oxidizer which contacts it in the alkaline above materials may be neutralized in other suitable coating. It adds to the alkaline above-mentioned material, and a reducing agent, i.e., sodium sulfite, a sodium thiosulfurous acid; anti-oxidant, i.e., BHA, BHT; and a transition metal especially iron, cobalt, nickel, and copper are contained in an active agent. Although the enzyme stability which these active agents are independent, can be used combining other reacting agents, or have a carrier, especially film forming property, and polymer which is water solubility, i.e., self, strengthened is not brought about, it may use together with what strengthens the fusibility of an active agent. When it is intrinsically put into an active agent into an inertness carrier, the positive protection for an enzyme is given.

The material which can be used as an active agent by this invention forms an effective barrier by various methods to the oxidizer of removal nature. A basic additive agent, for example, sodium carbonate, and a sodium silicate neutralize an acid oxidizer. A reducing agent, for example, sodium sulfite and sodium subsulfite, and an anti-oxidant, for example, BHA and BHT, are decreased by carrying out the chemical reaction of the effect of a removal nature oxidizer to it. A transition metal (namely, iron, cobalt, nickel, copper, and these mixtures) works so that the catalyst of the disassembly of an oxidizer may be carried out, therefore it protects an enzyme. A reducing agent, an anti-oxidant, and a transition metal may be used for enzyme coating by that either which is combined with a suitable carrier, combining an alkali metal silicate.

The suitable carrier for the active agent used here does not need to bring about the stability of an enzyme, when an active agent does not exist, but in order to be equal to decomposition by an oxidizer, it must be nonresponsiveness enough under existence of a protecting agent. There are water-soluble polymer, a surface-active agent/dispersing agent, and a basic material in a suitable carrier. In the example of water-soluble polymer, it is polyacrylic acid (brand-name

Alcosperse157A), a polyethylene glycol (Carbowax PEG4600), polyvinyl alcohol, a polyvinyl pyrrolidone, and Gantrez ES-225. There are a registered trademark and poly (methyl vinyl ether/maleic acid) monoethyl ester. There are Neodol\*\* of a wetting agent, for example, ShellChemical Company, and loam and Haas's Triton (it is both a non-ion system surface-active agent) in the example of the surface-active agent which finds out a use as a carrier.

the activity protecting agent which is alkaline -- alkali metal silicate and carbonate, especially silicic acid - and lithium carbonate, sodium, and potassium -- there are a sodium silicate and sodium carbonate most suitably. However, when using an alkali metal silicate as a protecting agent, it must warn to bring about sufficient fusibility. The modulus of a silicate determines the degree of meltable in the aquosity medium. Although a modulus (namely, ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$ ) gives suitable, the sodium silicate of 3.22:1, for example, PQ brand "N" sodium silicate, enzyme stability, only low fusibility is given under US washing condition. The sodium silicate of the modulus 2:1, for example, PQ brand "D" sodium silicate, gives both the stability admitted and sufficient fusibility. the thing suitable at this invention for use -- from the modulus 1:1 **about** up to 3:1 -- more -- suitable -- about 1:1 to 2.75:1 -- it is a sodium silicate of (noting that other additives to coating cannot be found) from 1.5:1 to 2.5:1 most suitably. However, a sodium silicate with a larger modulus than 3:1 can also be used especially when combined with additives, such as a reducing agent, for example, sodium sulfite etc. It seems that this additive changes the crystal structure of a silicate and makes coating fusibility more.

An alkali metal silicate or carbonate can be used with a water-soluble carrier, in order to secure sufficient water solubility. The mixture of an alkali metal silicate and (or) alkali metal carbonate may be used.

In the most suitable embodiment, 40 to 100% of a sodium silicate may exist in 60 to 100% of quantity more suitably 5 to 100% (weight) during coating. Similarly, 2 to 50% of sodium carbonate may exist in 4 to 25% of quantity more suitably 0 to 99% (weight) during coating. Sodium carbonate or 2 to 50% of the potassium can exist in 4 to 25% of quantity more suitably 0 to 99% (weight) during coating.

Other protecting agents give the effect of various various fusibility and stability. It seems that they will be washed if a little transition metals exist above, and they make disassembly of a peroxy acid cause in liquid. therefore, a transition metal -- under coating -- 1-2000 ppm -- suitable -- 2-1000 -- existence \*\*\*\*\* is generally more suitably preferred in the quantity of 50-500 ppm. since a reducing agent is not \*\*\*\*\*, it may exist a peroxy acid in 2 to 40% of quantity more suitably 1 to 60% (weight) during coating catalytically. **1 to 50% of** since similarly an anti-oxidant does not decompose a peroxy acid catalytically, either -- under coating -- 0.1 to 20% (weight) -- general -- 0.5-15 -- it may exist in 0.75 to 10% of quantity more ordinarily. Probably, change of the concentration of the active agent which helps fusibility will be clear to a person skilled in the art. The argument on the interaction of a transition metal and oxidizer various kinds is looked at by Bull Tin OBU the chemical society OBU Japan and 47:1162 besides M.W. Lister, Canadian journal-off chemistry, 34:479 (1956), and K. HAGAKAWA.

Partly, it depends for the quantity of the protection active agent taken to protect an enzyme on the character of an oxidizing bleach, an environmental temperature, relative humidity, and the length of reserve time expected. Moreover, the quantity of the protecting agent demanded during coating changes with the types of the protecting agent used or its combination.

A basic material, for example, an ant potash metal silicate, may exist at a minimum of 5% (weight), and it may constitute the principal part of coating, or may use it as coating alone. In coating material, a reducing agent is 0.1 to 60% (weight), is usually 1 to 50%, and may exist at 2 to 40% more ordinarily. an anti-oxidant -- the inside of coating material -- 0.1 to 20% (weight) -- common -- 0.5-15 -- it may exist at 0.75 to 10% more ordinarily. 1-2000 ppm of transition metals **2-1000 ppm of** may exist by the concentration of 50-500 ppm more ordinarily.

Especially a suitable thing is coating of the sodium silicate which is not accompanied by it or accompanied by sodium carbonate, and the transition metal exists by the concentration of 50-500 ppm.

An enzyme may be coated with arbitrary physical forms. Since the enzyme grain usually marketed can be mobilized and it can coat with a fluid bed spray coater, the convenient form for coating is given especially. Fig. 1 is a scanning microphotograph in which the particulate structure of an enzyme is shown. Fig. 3 \*\*\*\*s the enzyme of other forms which may be obtained commercially, it has the core carrier material 1, the enzyme layer 2, and the film layer 3, and a film layer serves to make the minimum the characteristic which an enzyme dust-izes. While the coating method in a fluid bed spray coater permits the economization of a reacting

agent, it brings about good covering of particles. an enzyme -- particle state or other shape -- for example, the mixing method, a spray method, and dip coating -- or it absorbs -- making (blotting) -- it may be coated. Probably the form of other coating will also be suitable for the enzyme of other forms, and it will be easily clear to a person skilled in the art. When required, in order to provide the enzyme surface to coating material, a wetting agent, a binder, for example, Neodol\*\*25-12, or 45-7 may be used.

Fig. 2 is a scanning electron micrograph in which the enzyme grain 2 is shown. The enzyme grain 2 is coated with PQ brand "D" sodium silicate. The coating 4 comprises about 25.5% of the weight of uncoated particles. The enzyme grain of Fig. 2 was coated with the atomization pneumatic pressure of 1.3 bars, and the floor temperature of 55 \*\* by 5g of rates-of-flow/using an EAROMA tick \*\* fluid bed and model STREA-1 at the time of fluidization air speed 130m<sup>3</sup>/min. Atomized coating comprises 15% of sodium silicate, and 85% of water. Average coating thickness was about 14 microns.

Fig. 4 is a typical sectional view showing the enzyme covered with the soluble protective coating 4 according to this invention.

A certain grade depends for the thickness of coating on the application art of coating. When the increase of weight was coated with an enzyme grain 15% using "D" sodium silicate solution, coating was an average of about 10-micron thickness. When the increase of 25% of weight was coated with the same enzyme grain by the same coating, it became coating of about 14-micron thickness on the average. Probably, coating changes from 15 to 30% (weight) to the whole 10 to 40% 5 to 100% suitably **of the weight of an uncoated enzyme / about 3 to 500% or it**. If coating thickness increases, it is distinct that the fusibility of an enzyme falls about given coating. Therefore, coating which covers or encapsulates particles thoroughly substantially is desirable, they are uniform and durability-like, and is easy to apply, Almost or completely do not produce the condensation of particles by which the coat was carried out, and suitable solubility is brought about in an aquosity medium, and it is bringing about coating which protects the activity of an enzyme suitably.

Suitable protection of an enzyme says the percentage of the active oxygen which remains after contacting an oxidizing bleach densely within the environment which the enzyme closed on these Descriptions. Since high heat and high relative humidity promote the denaturation of an enzyme, the stability of an enzyme is measured with 90 degrees F (32 \*\*) of facilities, and 85% relative humidity. the stability of the enzyme in which suitable stability was coated -- twice **at least** -- suitable -- 4 times -- and more suitably, after beyond four weeks or it, it comes out and is given by coating at a certain time. An experimental condition 20% of DPDDA, 9% of MgSO<sub>4</sub>, 10% of adipic acid, and 1% of binder, the DPDDA (diperoxydodecane JIOIKKU acid) grain to which the remainder changes from Na<sub>2</sub>SO<sub>4</sub> and water -- even if small, it includes mixing an enzyme with a peroxy acid bleaching compound with 20% (weight). The coated enzyme grain must bring about solubility sufficient in the bottom of a washing condition for an enzyme to be released easily in a detergent solution. A standard detergent solution is made by dissolving the 1.5-g Tide \*\* detergent (Procter & Gamble) in the water of 1\*\* at 20 \*\*. Generally, 90% of the particles containing an enzyme of each which was coated should dissolve, distribute or collapse within about 8 minutes less than about 12 minutes suitably less than about 15 minutes in the detergent solution which is about 20 \*\*.

The coated enzyme finds out a use to an oxidizing bleaching constituent. \*\* -- the example of typical combination of a bleaching constituent **like** is as follows.

example of combination -- A ingredient % of the weight peroxy-acid grain 1 - 80 pH regulation particles (boric acid) -- 1-5 -- enzyme grain 0.1-10 (by weight of the enzyme which is not carrying out a coat) coated

FWA particles -- example of charge bead of 0.5-10 aroma 0.1 - 2 bulking agent (Na<sub>2</sub>SO<sub>4</sub>)

residual combination -- B ingredient % of the weight peroxy-acid grain 1 - 50 pH regulation particles (boric acid) -- 10-50 -- enzyme grain 0.5-4 (by weight of the enzyme which is not carrying out a coat) coated

FWA particles -- charge bead of 0.5-5 aroma 0.1 - 1 -- example of bulking agent (Na<sub>2</sub>SO<sub>4</sub>)

residual combination -- the C ingredient % of the weight DPDDA 5 - 15 boric acid 7 - 20 FWA 0.1-1 -- enzyme grain 0.3-2 (by weight of the enzyme which is not carrying out a coat) coated Na<sub>2</sub>SO<sub>4</sub> emainder Illustration-like **the above-mentioned example of combination**. Other combination is also meant as long as it goes into the guideline of the oxidizing bleach / coating enzyme constituent of this invention. Weight % of the coated enzyme grain in combination is

dramatically changed with the weight of coating. Entering in 0.1 to 10% of range by the weight of the enzyme in which the amount of enzymes in combination generally is not coated is meant.

Suitable working example is accepted by the grain where the peroxy-acid bleach was stabilized, and the bleaching constituent in which the moisture content is carefully adjusted according to U.S. Serial Number 899,461 is given. A peroxy-acid grain and each enzyme grain produce the dry bleaching constituent which dry mixing is respectively carried out with other ingredients, and contains the coated enzyme grain.

Experiment Alkali metal silicate coating produces the husks of the fusibility which carries out the husk of the enzyme substantially, and this protects an enzyme from an oxidizing bleach. Using an additional protection active agent for this coating may make the coated stability or fusibility of an enzyme increase, and it may be decreased. That a protecting agent exists in a carrier will make the stability of the enzyme similarly increase only compared with a carrier, although the fusibility of an enzyme grain may be fluctuated. The next table 1 shows the stability and fusibility of various silicates, a carrier, and a reactive additive.

For drawings please refer to the original document.

Fusibility was measured with the standard detergent solution which added the 1.5-g Tide \*\* detergent (Procter & Gamble) at the water of 1\*\* in each case. A 20 ppm enzyme was examined among the solution. The weight of the enzyme before coating was adjusted according to the increase of weight of coating. The judgment thing was removed continuing churning. A 3-ml judgment thing was removed from the solution at intervals of 15 seconds per for 1 minute of the beginning in the 1.5 more, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 8, 10, 12, 15, 20 and 25, and 30 minutes. The contrast which is not coated was examined for every set of the sample coated in order to secure the correspondence nature of a value.

Stability was analyzed as follows. The borate salt buffer of 0.05M was filled 2/3 in the capacity flask of 1\*\*. 4-ml 1.5M Na<sub>2</sub>SO<sub>3</sub> was added and DPDDA was cooled. If a bubble comes out, 1 ml of additional cooling agents will be added at a stretch as occasion demands. A 10-g sample was added, and it is a borate salt buffer, and the flask was rinsed, and was agitated for 10 minutes. Subsequently, the mixture was diluted with the borate salt buffer to 1\*\*, and churning was continued for 5 minutes. An 8-ml solution was moved to the vial with the pipette, and an 8-ml additional buffer was added. Per **buffer 1\*\* / 0.075g Alcalase\*\*** is made now. 3 ml of diluted solution was put into the autoanalyzer for science with the pipette for every test sample for chemical analysis.

Unless it refused in particular, after the stability of the sample mixed the coated enzyme with the 20% of DPDDA grain content peroxy acid bleaching constituent, it was measured. It succeeded to this mixture and it carried out seal preservation at the 4 uncia double poly coating cardboard box.

The enzyme grain was coated with the atomization pneumatic pressure of 1.3 bars, and the floor temperature of 55 \*\* using EAROMA tick \*\* fluid floor model STREA-1 at the time of the 5g rate of flow for /, and fluidization air speed 130m<sup>3</sup>/.

"D" and the "N" sodium silicate point out "D" of PQ Corporation, and the "N" sodium silicate. example 1 An enzyme and a diperoxy pickling agent constituent are respectively put in in one container, however it was made not to make it contact physically mutually.

It put into the 20-ml vial which opened Alcalase\*\*2.0T 0.14-g sample. It put in the 8 uncia jar containing the diperoxyacid bleaching constituent which succeeds to this vial and follows said example C of combination. Subsequently, an 8 uncia jar was sealed and it saved for four weeks at 100 degrees F (37.8 \*\*). The enzyme activity of four weeks after was 53% of the activity of the original level. The control sample of Alcalase\*\*2.0T saved for four weeks at 100 degrees F within the closed vial showed 97% of enzyme activity of the original level.

This shows that just only detaching physically was not enough to protect an enzyme from the operation near the diperoxyacid bleaching constituent. In this way, the active agent which protects an enzyme is required in order to realize stability which can be accepted.

example 2 The shellac was used to coat a hydrolase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it was made to mobilize by the flow of the warm air (50-55 \*\*) at the time of abbreviation 100m<sup>3</sup>/ . The solution of the shellac was diluted with ethanol to solid content 18%, and the spray was carried out at 6-10g a rate for /by the nozzle to up to the mobilized enzyme. The temperature which was governing the inside of a turbulent flow exhaust

air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzyme had the following features. Coating occupied 22% of the weight of the enzyme which is not coated. Within the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 20 minutes, and showed 90% of solubility in 27 minutes. As for the stability in the diperoxyacid bleaching constituent of the coated enzyme, 46% of enzyme remained after two-week preservation by 90 degrees F/85%RH (relative humidity). The stability of the enzyme which is not coated with the bottom of the same conditions was 7.4%. Although this can obtain the stability which can be admitted, it shows that it becomes impossible to admit stability if coating is not chosen carefully.

example 3 The polyethylene glycol was used for coating of a hydrolase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 3g a rate for /by the nozzle to up to the enzyme which mobilized 20% of PEG Carbowax\*\* (Union Carbide) and 30% of water, and the solution of 50% of ethanol. The temperature which was governing the inside of a turbulent flow exhaust air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 20.6% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 0.75 minute, and showed 90% of solubility in 1.5 minutes. The stability in the diperoxyacid bleaching constituent of the coated enzyme was 13.8% of enzyme remains after two-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which was not coated was 7.4%.

This shows that mere physical separation is not enough to protect an enzyme from an oxidizing compound. It works so that an oxidizing compound may be neutralized, and the chemical barrier which gives the suitable fusibility for a detergent bleach is required.

example 4 Alcalase of four copies (weight) \*\*2.0T was added at 100 degrees F (37.8 \*\*) to Neodol of one copy \*\*45-7 (shell) within the beaker. It added until it became sodium carbonate of eight copies of total amounts, agitating one copy of sodium carbonate at a time violently at a stretch. Weight increase percentage was about 225% to the weight of an enzyme. It under the same conditions of the enzyme which is not coated compared with the stability of the enzyme coated with 100 degrees F four weeks afterward having been 83% in the dry bleaching constituent containing about 20% of peroxy-acid grain was 67%.

example 5 The sodium silicate of the modulus 2.00 was used for coating of a hydrolase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 7g a rate for /by the nozzle to up to the enzyme which diluted the "D" sodium silicate to solid content 25%, and mobilized it from 44% solid content with water. The temperature which was governing the inside of a turbulent flow exhaust air mixer was about 50 degrees. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 22.5% of the weight of the uncoated enzyme. In the detergent solution, in 2 minutes, when the granule was for 50% of solubility, and 4.5 minutes, it showed 90% of solubility at 20 \*\*. The stability under the same conditions of the enzyme which the stability of the coated enzyme is 74% of enzyme remains in four weeks, and is not coating it with 90 degrees F/85% relative humidity was 4%.

example 6 The transition metal was added to the sodium silicate of Example 5. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 6g a rate for /by the nozzle from on the enzyme which mobilized the thing for which "D" sodium silicate solution was made to contain 100 ppm copper (as copper sulfate), iron (as ferrous sulfate), cobalt (as cobalt sulfate), and nickel respectively (as nickel sulfate). The temperature which governed the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme constituent which flows easily was obtained and, subsequently it was coated. The coated enzyme occupied 22% of the weight of the enzyme which is not coated. The granule showed 50% of solubility in 2.5 minutes at 20 \*\* in the detergent solution, and showed 90% of solubility in 5.0 minutes. The stability under the same conditions of the enzyme which 87% of enzyme remained four weeks afterward, and the stability in the inside of the diperoxyacid bleaching constituent of the coated enzyme is not coating with 90 degrees F/85% relative humidity was 4%.

example 7 Sodium carbonate was added to the sodium silicate of Example 5.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow

of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 6g a rate for /by the nozzle to up to the enzyme which mobilized the solution which comprises 15% of "D" sodium silicate solid content, 10% of Na<sub>2</sub>CO<sub>3</sub>, and 75% of water. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme constituent which flows easily was obtained and, subsequently it was coated. The feature of the coated enzyme was as follows. Coating occupied 20.5% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 1.5 minutes, and showed 90% of solubility in 3.5 minutes. As for the stability in the dperoxyacid bleaching constituent of the coated enzyme, 66% of enzyme remained after four-week preservation with 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which is not coated was 4% remains.

example 8 Sodium sulfite (reducing agent) was added to the sodium silicate of Example 5. Alcalase\*\*2.0T of 200 was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . Sodium sulfite was melted in water. Subsequently, this was added to the "D" sodium silicate and it was considered as the solution containing 1.2% of "D" sodium silicate solid content, 8.4% of sodium sulfite, and 79% of water. The spray was carried out at 7g a rate for /by the nozzle to up to the enzyme which mobilized this solution. The temperature which governs the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme which flows easily was obtained and, subsequently this was coated. The coated enzyme had the following features. Coating occupied 17% of the weight of the uncoated enzyme. Coating was aimed at 60% of "D" sodium silicate and 40% of sodium sulfite being included. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 2 minutes, and showed 90% of solubility in 3 minutes. The stability in the dperoxyacid bleaching constituent of the coated enzyme was 68% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity.

example 9 The sodium silicate of the modulus 3.22 was used for coating of the hydase enzyme. Solubility fell remarkably compared with the sodium silicate of the modulus 2.0. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (45-50 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The "N" sodium silicate was diluted from solid content (at the time of purchase) with water to solid content 25% 44%. The spray was carried out at 5g a rate for /by the nozzle to up to the enzyme which mobilized this solution. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 35% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 55% of solubility in 11.5 minutes, and showed 90% of solubility in 20 minutes. The stability in the dperoxyacid bleaching constituent of the coated enzyme was 64% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which is not coated was 4%.

example 10 Polyvinyl alcohol was used as coating of a hydase enzyme. Although solubility was good, the stability after four-week preservation of an enzyme was not able to be admitted. Sodium lauryl sulfate was added for reduction with Neva.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (40 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 3g a rate for /by the nozzle to up to the enzyme which mobilized 4.9% of polyvinyl alcohol, 6.1% of sodium lauryl sulfate, 44.5% of water, and the solution of 44.5% of ethanol. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 35-40 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzymes were the following features. Coating occupied 9% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 1 minute, and showed 90% of solubility in 2 minutes. The stability in the dperoxyacid bleaching constituent of the coated enzyme showed 3.6% remains of the enzyme after four-week preservation with 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which is not coated was 4% remains.

example 11 When BHT (anti-oxidant) was added to polyvinyl alcohol of Example 10, enzyme stability increased remarkably.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it \*\*\*\*\*\*(ed) there with the flow of the warm air (40 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 4g a rate for /through the nozzle to up to the enzyme which mobilized 4.44% of polyvinyl

alcohol, 5.56% of sodium lauryl sulfate, 0.1% of BHT, 44.5% of water, and the solution containing 44.9% of ethanol. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 35-40 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzymes were the following features. Coating occupied 10.5% of the weight of the uncoated enzyme. Coating was aimed at comprising 44% of polyvinyl alcohol, 55% of sodium lauryl sulfate, and 1% of BHT. The stability in the diperoxyacid bleaching constituent of the coated enzyme was 32% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of an uncoated enzyme was 4% remains.

example 12 As another example, the silicate was used for encapsulating an enzyme combining a transition metal. Subsequently, this capsule was mixed with the dry bleaching constituent which uses sodium percarbonate as a base. In the above-mentioned examples 5-6, similarly, 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized by the flow of the warm air (50-55 \*\*) at the time of rate-of-flow abbreviation 130m<sup>3</sup>/ Every 100 ppm copper (as CuSO<sub>4</sub>), iron (as FeSO<sub>4</sub>), The spray was carried out at 6g a rate for /through the nozzle to up to the enzyme which mobilized the "D" sodium silicate for which cobalt (as CoSO<sub>4</sub>) and nickel are contained (as NiSO<sub>4</sub>). Subsequently, the letter enzyme mixture of a flow was coated. Coating occupied 22% of the weight of the uncoated enzyme as in Example 6. The enzyme in which the stability of the enzyme in the dry bleach of a percarbonate base remains after four-week preservation with 90 degrees F/85% relative humidity was 89%. A percarbonate constituent 54.6% of Na<sub>2</sub>CO<sub>3</sub>, 43.96% of percarbonate, 0.68% of Tinopal 5 BMX-C (a fluorescence white agent, Ciba-Geigy), 0.48% of charge of aroma, and 0.28% of TritonX-100 (a non-ion system surface-active agent -- anti- -- powdering -- an agent) were comprised. Although the stability (with no transition metal) of the coated enzyme was good, it was \*\*\*\*\* (about 79%) stability per same period. Un-coating Alcalase was poor stability (19%) per same period. About long-term stability, the alcalase coated with both the silicate and the transition metal showed stability with 24 good weeks under the same temperature/relative humidity. That is, it is about 73%. Remains activity was 52% and 58%, respectively about the 24 weeks when the alcalase coated only with the silicate and uncoated alcalase are the same. The stability of Milezyme\*\* was as low as about 2%. This is shown to Fig. 5 by the graph. As mentioned above, although the constituent useful as a domestic bleach was explained, this invention also has intention of change and correction which enter within the limits of it.

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### **Field of the Invention**

This invention relates to a cloth bleach for home use, more specifically uses an oxidizing bleach, especially an organic peroxy acid bleach as base resin, and relates to the dry bleaching constituent containing an enzyme. An enzyme exists as various grain coated in order to strengthen the stability in a bleaching constituent. Coating of an enzyme contains one sort or the active agent beyond it which protects an enzyme from degradation by a bleaching constituent.

### **Background of the Invention**

The bleaching constituent is used at the home for bleaching of cloth, and wash for years. Since it is cheap and validity is high, and manufacture is easy and stable, the liquefied bleach based on a hypochlorite compound is used widely. However, new requirements go also into bleaching art by the appearance of modernistic synthetic dye, and use of a modernistic automatic washing machine, and the necessity for the bleaching constituent of a different type is produced. In order to fulfill this necessity, and in order to develop the use of a bleach for home use widely, a bleach system different in recent years is introduced.

It is the dry bleaching constituent based on the peroxy acid compound that he is interested especially in recent years. A peroxy-acid compound is a chemical functional group.  
For drawings please refer to the original document.

It has high oxidation capacity by one \*\* or existence beyond it.

It is desirable similarly to prepare one sort or the enzyme beyond it for the purpose of dirt removal in addition to an activity oxidizer. By cleaving to the monomer or oligomer of low molecular weight which dissolves the dirt residue of the amount of Polymer Division in a wash

medium easily, an enzyme degrades dirt of a certain kind and silverfish, and has the capability to promote removal or to transform a substrate to other refining things. An enzyme has an advantage of substrate specificity, i.e., an enzyme attacks only a unique combination and it does not have chemical influence on the substance which should usually be washed. \*\* -- the example of an enzyme **like** is an enzyme which can hydrolyze dirt, and is chosen from the enzyme group classified according to International union OBU biochemistry as "hydrase." Protease, amylase, lipase, and cellulase are classified into hydrase.

\*\*\*\* in which an enzyme denaturalizes easily by a harsh environment (molecular structure is changed) -- it is sensitive protein and a certain change can repeal an enzyme. If a strong acid voltinism bleach like organic acid peroxide has an oxidizing bleaching constituent of a certain concentration in the warm damp environment especially, it is harmful to the stability of an enzyme.

Various methods for stabilizing an enzyme and bringing about a good mixture with an enzyme, a detergent, or a bleach are proposed. an enzyme is variously looked like **carriers, such as clay, starch, and amine-ized polysaccharide**, , and they adhere to it, and it agglutinates a detergent carrier -- even having -- it is. Extrusion of the enzyme is granulated and carried out, and a husk is carried out to a film, and it can give a coloring-ized agent. In order to strengthen the stability of an enzyme, the trial which mixes an enzyme with protein, lowers the relative humidity of storage environment, divides a bleach into separate grain, or adds a reducing agent and a buffer for pH is made. However, especially the instability of the enzyme in a peroxy acid bleaching constituent is still continuing bringing about difficulty in the mothball of the peroxy bleaching constituent in which the bleach is densely mixed with the enzyme.

#### **Summary of the Invention**

This invention relates to an enzyme content oxidizing bleaching constituent, especially the bleaching constituent based on organic 2 peroxy acid (JIPERU acid). More concretely, while this constituent supports the fusibility of an enzyme, it brings about the stability of an enzyme during the mothball under existence of an oxidizer.

An improvement constituent is prepared by coating or encapsulating an enzyme with the material which brings about sufficient fusibility, when an enzyme is effectively made into a tolerance \*\*\*\* thing to degradation in a bleaching constituent and it puts in an aquosity medium which is seen during wash. Especially an alkaline material works as a protecting agent, and before it contacts an enzyme and denatures an oxidizer, it is carbonated. \*\* -- the examples of a protecting agent **like** are a sodium silicate and sodium carbonate.

These both block the erosion to the enzyme by an oxidizer physically, and carbonate an oxidizer chemically.

What forbids radical chain oxidation of anti-oxidants, for example, BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), etc., such as a reducing agent, for example, sodium sulfite, and sodium subsulfite, again is contained in activity protection. A transition metal especially iron, cobalt, nickel, and copper work as a catalyst which brings destruction of an oxidizer forward, therefore protect an enzyme. These active oxygen protecting agents can be used with a carrier and the water-soluble polymer which commits fusibility as a dispersing agent or carriers for strength and a protecting agent although an enzyme is not especially protected by itself.

A standard bleaching constituent additive agent, for example, a builder, an extender, a buffer, a brightening agent, an aromatic, etc. can be added to individual enzyme grain and an oxidizing bleach, and can be included in an enzyme content oxidizing bleaching constituent.

Therefore, the purpose of this invention is to provide the enzyme protected from denaturation in the constituent containing an oxidizing bleach.

Other purposes of this invention are to provide the coated enzyme which is fusibility in an aquosity medium.

Other purposes of this invention are to provide the oxidizer bleaching constituent containing the enzyme in which the stability under preservation was enhanced.

The purpose of further others of this invention is to bring about the enzyme stable in the enzyme content peroxy-acid bleaching constituent.

#### **A concrete indication of an invention**

Unless it refuses in particular by the following, all the percentage, a ratio, or a part is based on weight.

Enzyme An enzyme is a publicly known additive to the ordinary constituent containing especially a detergent and a bleach, and by eroding dirt and silverfish, it works so that the cleaning effect of a detergent may be improved. The enzyme is sold in the form of the grain and

the round or needlelike small aggregate.

The section of the grain (prill) of an enzyme is shown in the microphotograph of Fig. 1. When such a grain was added in a traditional dry detergent, it was tended to separate this enzyme from a detergent mixture. Granulating an enzyme as this difficult solution, i.e., make an enzyme adhere to carriers, such as starch or clay (granulation) or carrying out the spray of the enzyme directly on a solid detergent composition were performed. Such art was suitable about the comparatively mild dry detergent composition known in the past. However, it is not admitted that this granulation art is suitable to protect an enzyme from degradation by a more powerful new oxidizing bleaching constituent.

The enzyme which can hydrolyze a substrate, for example, dirt, is used for a usually mild bleaching constituent. The name received by the International union OBU biochemistry of these enzymes is hydrolase. In hydrolase, not limitation but protease (a protein system substrate is digested), Amylase (it is known also as carbohydrolase and carbohydrate is digested), lipase (it is known also as esterase and a fat is digested), cellulase (cellulose type polysaccharide is digested), and these mixtures are contained.

Protease, especially alkaline protease are preferred to use by this invention. Since alkaline protease makes fusibility more the blood which especially hydrolyzes a protein substrate and becomes a problem, and herbal dirt, it is useful for especially a wash use.

Commercial alkaline protease. It is led by various races of bacteria (*Bacillus subtilis*). These protease is known also as the subdust gin (subtilisins) again. For the un-restrictive example of this, brand name Esperase\*\*, Savinase\*\*, and -- as Alcalase\*\* -- Novo industry A/S (Denmark.) protease and brand name Maxatase\*\* and Maxacal\*\* which can be obtained from Bug Suva Held -- Gist BUROKADESUN.V (the Netherlands.) There are a thing currently sold from Delft and a thing which is sold from Miles Laboratories (State Elkhart of Indiana), and is by brand name Milezyme\*\* APL. The mixture of an enzyme is also included in this invention. Also refer to US,4,511,490,B (SUTANISU Lossky etc.).

Commercial protease is supplied as a grain (prill), a granular material, or a ground enzyme. Stabilizer, for example, triethanolamine, clay, or starch can be included in these enzymes. In addition to protease, other enzymes can also be replaced with, and it can be used for this constituent. Lipase and amylase can find out a use to this constituent. Lipase is written in three columns of 15-55 lines of US,3,950,277,B. The description is used here. To suitable amylase, Rapidase\*\* (from SOSHIETE RAPIDAZE of France), There are Maxamyl\*\* (from Gist BUROKADESUN.V), Termamyl\*\* (from Novo industry A/S), and Milezyme\*\* DAL (from Miles Laboratories). Although cellulase is also mixed, it is desirable, and the US,4,479,881,B (Thailand), No. 4,443,355 (MURATA etc.), No. 4,435,307 (BABESU guard etc.), and No. 3,983,002 (OYA etc.) description is used.

A suitable enzyme level to use it by this invention is from about 0.1% from 0.4% to 2% most suitably 3% in 0.25% 10% based on the enzyme which is not coated.

Oxidizing bleach An enzyme tends to receive degradation by heat, humidity, and chemical action. If especially an enzyme contacts a strong oxidizer, it will denaturalize quickly. Generally a Prior art (granulation), for example, granulation, is not enough within a strong acid voltmism constituent which is based on a dry hypochlorite and a peroxy acid bleach to protect an enzyme. Moreover, the compound which generates hydrogen peroxide within an aquosity medium tends to have an operation harmful to the enzyme under preservation. There are an alkaline metal perboric acid salt (sodium perborate monohydrate or four hydrates), percarbonate (sodium percarbonate), and various hydrogen peroxide adducts in such a compound.

an oxidizing bleach -- general -- the inside of an aquosity medium -- about 0.1 to 50 ppm A.O. (active oxygen) -- more generally about 0.1 to 30 ppm A.O. is given. A. The analysis of O. and a description are looked at by a "par acid and peroxide oxy day SHONZU" oxidation and pp 213-258 (1968) (Dr. S N Lewis). This description is used here.

An organic JI peroxy acid is a good oxidizer, and is known for the industry as a useful bleach. An organic interesting JI peroxy acid may be compounded from much long chain diacid.

US,4,337,213,B (June 29, 1982, MARINOUSUKI, etc.) has indicated manufacture of the peroxy acid by making selected acid react to H<sub>2</sub>O under existence of H<sub>2</sub>SO<sub>4</sub>.

An organic JI peroxy acid has the following general structure.

For drawings please refer to the original document.

here -- R -- 4-20 carbon atom -- they are the straight chain alkyls from 6 to 12 more suitably. Especially a suitable thing is diperoxydodecane JIOIKKU acid (DPDDA). -- here -- R --  $(\text{CH}_2)^{10}$  And JIPERU azelaic acid (DPAA) -- here -- R --  $_{7}(\text{OH}_2)$  -- it is .

It is for the detergent bleach containing peroxy acid also containing the exothermic depressant generally, and this protecting a peroxy acid bleach from febrile degradation by controlling the quantity of the existing water. A typical exothermic depressant is hydrated salt, for example, a  $\text{MgSO}_4/\text{Na}_2\text{SO}_4$  mixture. combining peroxy acid and an exothermic depressant in a granule -- \*\* -- making the stability of the enzyme which exists in a constituent increase is found out by adjusting the water content of a granule like carefully. Refer to U.S. Serial Number 899,461 under simultaneous pendency. The oxidizers of useful others are sodium perborate monohydrate and four hydrates, and sodium percarbonate in this invention.

Other additive components The additive component determined by the use of a constituent and preservation may be added by the bleach-enzyme constituent of this invention. The bleaching constituent is indicated by the simultaneous pendency U.S. application No. (August 12, 1986 application) 899,461.

The organic dicarboxylic acid of general formula  $\text{HOOC-R'-COOH}$  ( $\text{R}'$  is the carbon atoms from 1 to 10 here, and adipic acid is  $\text{R}'=(\text{CH}_2)_4$ , for example) is an additive agent desirable to a detergent bleaching constituent. \*\* -- organic acid like has the work which will dilute a JI peroxy acid (supposing it exists), and when using bleaching output, it helps the pH adjustment of wash water.

a JI peroxy acid -- an exothermic depressant -- and when it exists with a granular form with organic acid, especially the thing for which the physical integrity of grain is maintained is arbitrarily desirable by using a cementitious material. Such a material has the work which prevents a bleach's becoming powder during conveyance and handling, or being divided. Especially, the polymer acid which is not carbonated is interesting, and if this is used, per diperoxyacid in a detergent bleaching agent composition, an unpleasant smell of a thing can be decreased substantially or it can remove it.

Since the opposite operation of the fluorescence white agent (FWA) is carried out at yellowing of cotton and synthetic transition, it is an ingredient desirable although included in a bleaching constituent. FWA is absorbed by cloth in wash and (or) a bleaching process. FWA absorbs ultraviolet rays and functions by pouring this and making light emit as visible light of the blue wavelength range generally. The light of this result produces the glossy whitening effect, and carries out the operation which negates yellowing or the muddiness of cloth which this bleached. Such FWA can be commercially obtained with the trade name of "Tinopal" from Ciba-Geigy Corporation (Switzerland, BEZERU). Same FWA is indicated by the U.S. Pat. No. 3,393,153 item (gin MARA etc.). This description is used here.

In order to give protection of FWA -- an alkaline diluent (it protects from oxidation), and a cementitious material -- and it is arbitrarily mixable with bulking material, for example,  $\text{Na}_2\text{SO}_4$ , and a coloring matter. Subsequently, a mixture is compressed, particles (particle) are made and this is mixed with a bleaching constituent. The FWA particle can constitute about 0.5 to 10% of bleaching constituents (weight).

Generally the aromatic which gives a pleasant scent to a bleaching constituent is contained. Whether since an aromatic tends to receive oxidation by a bleach, it is encapsulated with polymer materials, such as polyvinyl alcohol, starch, or sugar is made to absorb an aromatic, and it may be protected by whether this is fabricated in a bead. Since these aromatic bead is fusibility at water, when a bleaching constituent is melted in water, an aromatic is released, but the aromatic is protected from oxidation by a bleach during preservation.

An aromatic is used also for giving a \*\*\*\* scent to the upper space of the container into which the bleach is put again. For example, refer to US,4,858,758,B (Mitchell etc.).

A buffer, a builder, and (or) a bulking agent may also be made to exist in a bleaching constituent. Boric acid and (or) the sodium borate are suitable to carry out of a constituent pH \*\*\*\*\*. Sodium carbonate, sodium bicarbonate, and other alkaline buffers are one of other buffers. A builder has organic builders, such as a sodium silicate and potassium, sodium phosphate, sodium tripolyphosphate, sodium tetrapolyphosphate, aluminosilicate (ZEORATO), and sodium sulfo succinate. A bulking agent can also be included. The most suitable bulking agent is sodium sulfate. A buffer and a bulking agent are granular and are added so that the whole constituent may turn into a drying constituent which carries out a dry flow. . 5 to 90% (weight) of range of a constituent may be sufficient as a buffer, and an another side builder and

(or) a bulking agent are also 90% of ranges, and obtain them from about 5%. Coated enzyme The coated enzyme is prepared whether an enzyme is substantially coated with the material which permits sufficient fusibility thoroughly, and by encapsulating, when an enzyme is made into a tolerance \*\*\*\* thing at oxidation of a bleach and it puts into an aquosity medium. Various categories are among the active agents which protect the enzyme contained in coating. That is, they are alkalinity or neutral material, a reducing agent, an anti-oxidant, and a transition metal. These each may be used with other active agents of a category which is the same or is different. In a suitable embodiment, a reducing agent, an anti-oxidant, and (or) a transition metal are especially contained in coating which consists of an alkali metal silicate and (or) alkali metal carbonate in superior.

The most suitable coating also serves as a chemical barrier by neutralizing positively the oxidizer which a physical barrier is made to the attack by an oxidizer, and can be eliminated. the base (alkali) nature material exceeding pH about 11 -- more -- suitable -- the alkali metal silicate of pH 12 to 14 especially a sodium silicate, and \*\* -- the mixture with a silicate, alkali metal carbonate or bicarbonate, especially sodium carbonate brings about such suitable coating. ~~like~~ since the mixture with a silicate, this and carbonate, or bicarbonate forms a uniform vitrified matrix when the aquosity dispersion liquid are applied to the core of an enzyme -- especially -- \*\* -- it seems that it is better. this -- coating -- an effect -- oh, the necessity for the carrier material to close is abolished -- I will come out. The addition of alkali metal carbonate or bicarbonate can improve the fusibility of enzyme coating. \*\* -- the level in carbonate ~~like~~ or the silicate of bicarbonate can be adjusted so that the desired stability / soluble feature may be realized. pH of a salt or its mixture is measured as 10% solution of the salt.

There are some which were combined with one sort or the active agent beyond it which reacts chemically so that the oxidizer which contacts it in the alkaline above materials may be neutralized in other suitable coating. It adds to the alkaline above-mentioned material, and a reducing agent, i.e., sodium sulfite, a sodium thiosulfurous acid; anti-oxidant, i.e., BHA, BHT; and a transition metal especially iron, cobalt, nickel, and copper are contained in an active agent. Although the enzyme stability which these active agents are independent, can be used combining other reacting agents, or have a carrier, especially film forming property, and polymer which is water solubility, i.e., self, strengthened is not brought about, it may use together with what strengthens the fusibility of an active agent. When it is intrinsically put into an active agent into an inertness carrier, the positive protection for an enzyme is given. The material which can be used as an active agent by this invention forms an effective barrier by various methods to the oxidizer of removal nature. A basic additive agent, for example, sodium carbonate, and a sodium silicate neutralize an acid oxidizer. A reducing agent, for example, sodium sulfite and sodium subsulfite, and an anti-oxidant, for example, BHA and BHT, are decreased by carrying out the chemical reaction of the effect of a removal nature oxidizer to it. A transition metal (namely, iron, cobalt, nickel, copper, and these mixtures) works so that the catalyst of the disassembly of an oxidizer may be carried out, therefore it protects an enzyme. A reducing agent, an anti-oxidant, and a transition metal may be used for enzyme coating by that either which is combined with a suitable carrier, combining an alkali metal silicate.

The suitable carrier for the active agent used here does not need to bring about the stability of an enzyme, when an active agent does not exist, but in order to be equal to decomposition by an oxidizer, it must be nonresponsiveness enough under existence of a protecting agent. There are water-soluble polymer, a surface-active agent/dispersing agent, and a basic material in a suitable carrier. In the example of water-soluble polymer, it is polyacrylic acid (brand-name Alcosperse157A), a polyethylene glycol (Carbowax PEG4600), polyvinyl alcohol, a polyvinyl pyrrolidone, and Gantrez ES-225. There are a **registered trademark and poly (methyl vinyl ether/maleic acid) monoethyl ester**. There are Neodol\*\* of a wetting agent, for example, ShellChemical Company, and loam and Haas's Triton (it is both a non-ion system surface-active agent) in the example of the surface-active agent which finds out a use as a carrier.

the activity protecting agent which is alkaline -- alkali metal silicate and carbonate, especially silicic acid - and lithium carbonate, sodium, and potassium -- there are a sodium silicate and sodium carbonate most suitably. However, when using an alkali metal silicate as a protecting agent, it must warn to bring about sufficient fusibility. The modulus of a silicate determines the degree of meltable in the aquosity medium. Although a modulus (namely, ratio of  $\text{SiO}_2:\text{Na}_2\text{O}$ ) gives suitable, the sodium silicate of 3.22:1, for example, PQ brand "N" sodium silicate, enzyme stability, only low fusibility is given under US washing condition. The sodium silicate of the

modulus 2:1, for example, PQ brand "D" sodium silicate, gives both the stability admitted and sufficient fusibility. the thing suitable at this invention for use -- from the modulus 1:1 **about** up to 3:1 -- more -- suitable -- about 1:1 to 2.75:1 -- it is a sodium silicate of (noting that other additives to coating cannot be found) from 1.5:1 to 2.5:1 most suitably. However, a sodium silicate with a larger modulus than 3:1 can also be used especially when combined with additives, such as a reducing agent, for example, sodium sulfite etc. It seems that this additive changes the crystal structure of a silicate and makes coating fusibility more.

An alkali metal silicate or carbonate can be used with a water-soluble carrier, in order to secure sufficient water solubility. The mixture of an alkali metal silicate and (or) alkali metal carbonate may be used.

In the most suitable embodiment, 40 to 100% of a sodium silicate may exist in 60 to 100% of quantity more suitably 5 to 100% (weight) during coating. Similarly, 2 to 50% of sodium carbonate may exist in 4 to 25% of quantity more suitably 0 to 99% (weight) during coating. Sodium carbonate or 2 to 50% of the potassium can exist in 4 to 25% of quantity more suitably 0 to 99% (weight) during coating.

Other protecting agents give the effect of various various fusibility and stability. It seems that they will be washed if a little transition metals exist above, and they make disassembly of a peroxy acid cause in liquid. therefore, a transition metal -- under coating -- 1-2000 ppm -- suitable -- 2-1000 -- existence \*\*\*\*\* is generally more suitably preferred in the quantity of 50-500 ppm. since a reducing agent is not \*\*\*\*\*, it may exist a peroxy acid in 2 to 40% of quantity more suitably 1 to 60% (weight) during coating catalytically. **1 to 50% of** since similarly an anti-oxidant does not decompose a peroxy acid catalytically, either -- under coating -- 0.1 to 20% (weight) -- general -- 0.5-15 -- it may exist in 0.75 to 10% of quantity more ordinarily. Probably, change of the concentration of the active agent which helps fusibility will be clear to a person skilled in the art. The argument on the interaction of a transition metal and oxidizer various kinds is looked at by Bull. Tin OBU the chemical society OBU Japan and 47:1162 besides M.W. Lister, Canadian journal-off chemistry, 34:479 (1956), and K. HAGAKAWA.

Partly, it depends for the quantity of the protection active agent taken to protect an enzyme on the character of an oxidizing bleach, an environmental temperature, relative humidity, and the length of reserve time expected. Moreover, the quantity of the protecting agent demanded during coating changes with the types of the protecting agent used or its combination.

A basic material, for example, an ant potash metal silicate, may exist at a minimum of 5% (weight), and it may constitute the principal part of coating, or may use it as coating alone. In coating material, a reducing agent is 0.1 to 60% (weight), is usually 1 to 50%, and may exist at 2 to 40% more ordinarily. an anti-oxidant -- the inside of coating material -- 0.1 to 20% (weight) -- common -- 0.5-15 -- it may exist at 0.75 to 10% more ordinarily. 1-2000 ppm of transition metals **2-1000 ppm of** may exist by the concentration of 50-500 ppm more ordinarily.

Especially a suitable thing is coating of the sodium silicate which is not accompanied by it or accompanied by sodium carbonate, and the transition metal exists by the concentration of 50-500 ppm.

An enzyme may be coated with arbitrary physical forms. Since the enzyme grain usually marketed can be mobilized and it can coat with a fluid bed spray coater, the convenient form for coating is given especially. Fig. 1 is a scanning microphotograph in which the particulate structure of an enzyme is shown. Fig. 3 \*\*\*\*s the enzyme of other forms which may be obtained commercially, it has the core carrier material 1, the enzyme layer 2, and the film layer 3, and a film layer serves to make the minimum the characteristic which an enzyme dust-izes. While the coating method in a fluid bed spray coater permits the economization of a reacting agent, it brings about good covering of particles. an enzyme -- particle state or other shape -- for example, the mixing method, a spray method, and dip coating -- or it absorbs -- making (blotting) -- it may be coated. Probably the form of other coating will also be suitable for the enzyme of other forms, and it will be easily clear to a person skilled in the art. When required, in order to provide the enzyme surface to coating material, a wetting agent, a binder, for example, Neodol\*\*25-12, or 45-7 may be used.

Fig. 2 is a scanning electron micrograph in which the enzyme grain 2 is shown. The enzyme grain 2 is coated with PQ brand "D" sodium silicate. The coating 4 comprises about 25.5% of the weight of uncoated particles. The enzyme grain of Fig. 2 was coated with the atomization pneumatic pressure of 1.3 bars, and the floor temperature of 55 \*\* by 5g of rates-of-flow/using an EAROMA tick \*\* fluid bed and model STREA-1 at the time of fluidization air speed 130m<sup>3</sup>/ Atomized coating comprises 15% of sodium silicate, and 85% of water. Average coating

thickness was about 14 microns.

Fig. 4 is a typical sectional view showing the enzyme covered with the soluble protective coating 4 according to this invention.

A certain grade depends for the thickness of coating on the application art of coating. When the increase of weight was coated with an enzyme grain 15% using "D" sodium silicate solution, coating was an average of about 10-micron thickness. When the increase of 25% of weight was coated with the same enzyme grain by the same coating, it became coating of about 14-micron thickness on the average. Probably, coating changes from 15 to 30% (weight) to the whole 10 to 40% 5 to 100% suitably **of the weight of an uncoated enzyme / about 3 to 500% or it**. If coating thickness increases, it is distinct that the fusibility of an enzyme falls about given coating. Therefore, coating which covers or encapsulates particles thoroughly substantially is desirable, they are uniform and durability-like, and is easy to apply, Almost or completely do not produce the condensation of particles by which the coat was carried out, and suitable solubility is brought about in an aquosity medium, and it is bringing about coating which protects the activity of an enzyme suitably.

Suitable protection of an enzyme says the percentage of the active oxygen which remains after contacting an oxidizing bleach densely within the environment which the enzyme closed on these Descriptions. Since high heat and high relative humidity promote the denaturation of an enzyme, the stability of an enzyme is measured with 90 degrees F (32 \*\*) of facilities, and 85% relative humidity, the stability of the enzyme in which suitable stability was coated -- twice at least -- suitable -- 4 times -- and more suitably, after beyond four weeks or it, it comes out and is given by coating at a certain time. An experimental condition 20% of DPDDA, 9% of MgSO<sub>4</sub>, 10% of adipic acid, and 1% of binder, the DPDDA (diperoxydodecane JIOIKKU acid) grain to which the remainder changes from Na<sub>2</sub>SO<sub>4</sub> and water -- even if small, it includes mixing an enzyme with a peroxy acid bleaching compound with 20% (weight). The coated enzyme grain must bring about solubility sufficient in the bottom of a washing condition for an enzyme to be released easily in a detergent solution. A standard detergent solution is made by dissolving the 1.5-g Tide \*\* detergent (Procter & Gamble) in the water of 1\*\* at 20 \*\*. Generally, 90% of the particles containing an enzyme of each which was coated should dissolve, distribute or collapse within about 8 minutes less than about 12 minutes suitably less than about 15 minutes in the detergent solution which is about 20 \*\*.

The coated enzyme finds out a use to an oxidizing bleaching constituent. \*\* -- the example of typical combination of a bleaching constituent like is as follows.

example of combination -- A ingredient % of the weight peroxy-acid grain 1 - 80 pH regulation particles (boric acid) -- 1-5 -- enzyme grain 0.1-10 (by weight of the enzyme which is not carrying out a coat) coated

FWA particles -- example of charge bead of 0.5-10 aroma 0.1 - 2 bulking agent (Na<sub>2</sub>SO<sub>4</sub>)

residual combination -- B ingredient % of the weight peroxy-acid grain 1 - 50 pH regulation particles (boric acid) -- 10-50 -- enzyme grain 0.5-4 (by weight of the enzyme which is not carrying out a coat) coated

FWA particles -- charge bead of 0.5-5 aroma 0.1 - 1 -- example of bulking agent (Na<sub>2</sub>SO<sub>4</sub>)

residual combination -- the C ingredient % of the weight DPDDA 5 - 15 boric acid 7 - 20 FWA 0.1-1 -- enzyme grain 0.3-2 (by weight of the enzyme which is not carrying out a coat) coated Na<sub>2</sub>SO<sub>4</sub> emainder Illustration-like **the above-mentioned example of combination**. Other combination is also meant as long as it goes into the guideline of the oxidizing bleach / coating enzyme constituent of this invention. Weight % of the coated enzyme grain in combination is dramatically changed with the weight of coating. Entering in 0.1 to 10% of range by the weight of the enzyme in which the amount of enzymes in combination generally is not coated is meant.

Suitable working example is accepted by the grain where the peroxy-acid bleach was stabilized, and the bleaching constituent in which the moisture content is carefully adjusted according to U.S. Serial Number 899,461 is given. A peroxy-acid grain and each enzyme grain produce the dry bleaching constituent which dry mixing is respectively carried out with other ingredients, and contains the coated enzyme grain.

Experiment Alkali metal silicate coating produces the husks of the fusibility which carries out the husk of the enzyme substantially, and this protects an enzyme from an oxidizing bleach. Using an additional protection active agent for this coating may make the coated stability or fusibility of an enzyme increase, and it may be decreased. That a protecting agent exists in a

carrier will make the stability of the enzyme similarly increase only compared with a carrier, although the fusibility of an enzyme grain may be fluctuated. The next table 1 shows the stability and fusibility of various silicates, a carrier, and a reactive additive.

For drawings please refer to the original document.

Fusibility was measured with the standard detergent solution which added the 1.5-g Tide \*\* detergent (Procter & Gamble) at the water of 1\*\* in each case. A 20 ppm enzyme was examined among the solution. The weight of the enzyme before coating was adjusted according to the increase of weight of coating. The judgment thing was removed continuing churning. A 3-ml judgment thing was removed from the solution at intervals of 15 seconds per for 1 minute of the beginning in the 1.5 more, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 8, 10, 12, 15, 20 and 25, and 30 minutes. The contrast which is not coated was examined for every set of the sample coated in order to secure the correspondence nature of a value.

Stability was analyzed as follows. The borate salt buffer of 0.05M was filled 2/3 in the capacity flask of 1\*\*. 4-ml 1.5M Na<sub>2</sub>SO<sub>3</sub> was added and DPDDA was cooled. If a bubble comes out, 1 ml of additional cooling agents will be added at a stretch as occasion demands. A 10-g sample was added, and it is a borate salt buffer, and the flank was rinsed, and was agitated for 10 minutes. Subsequently, the mixture was diluted with the borate salt buffer to 1\*\*, and churning was continued for 5 minutes. An 8-ml solution was moved to the vial with the pipette, and an 8-ml additional buffer was added. Per **buffer 1\*\* / 0.075g Alcalase\*\*** is made now. 3 ml of diluted solution was put into the autoanalyzer for science with the pipette for every test sample for chemical analysis.

Unless it refused in particular, after the stability of the sample mixed the coated enzyme with the 20% of DPDDA grain content peroxy acid bleaching constituent, it was measured. It succeeded to this mixture and it carried out seal preservation at the 4 uncia double poly coating cardboard box.

The enzyme grain was coated with the atomization pneumatic pressure of 1.3 bars, and the floor temperature of 55 \*\* using EAROMA tick \*\* fluid floor model STREA-1 at the time of the 5g rate of flow for /, and fluidization air speed 130m<sup>3</sup>/.

"D" and the "N" sodium silicate point out "D" of PQ Corporation, and the "N" sodium silicate. example 1 An enzyme and a diperoxy pickling agent constituent are respectively put in in one container, however it was made not to make it contact physically mutually.

It put into the 20-ml vial which opened Alcalase\*\*2.0T 0.14-g sample. It put in the 8 uncia jar containing the diperoxyacid bleaching constituent which succeeds to this vial and follows said example C of combination. Subsequently, an 8 uncia jar was sealed and it saved for four weeks at 100 degrees F (37.8 \*\*). The enzyme activity of four weeks after was 53% of the activity of the original level. The control sample of Alcalase\*\*2.0T saved for four weeks at 100 degrees F within the closed vial showed 97% of enzyme activity of the original level.

This shows that just only detaching physically was not enough to protect an enzyme from the operation near the diperoxyacid bleaching constituent. In this way, the active agent which protects an enzyme is required in order to realize stability which can be accepted.

example 2 The shellac was used to coat a hydrolase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it was made to mobilize by the flow of the warm air (50-55 \*\*) at the time of abbreviation 100m<sup>3</sup>/. The solution of the shellac was diluted with ethanol to solid content 18%, and the spray was carried out at 6-10g a rate for /by the nozzle to up to the mobilized enzyme. The temperature which was governing the inside of a turbulent flow exhaust air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzyme had the following features. Coating occupied 22% of the weight of the enzyme which is not coated. Within the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 20 minutes, and showed 90% of solubility in 27 minutes. As for the stability in the diperoxyacid bleaching constituent of the coated enzyme, 46% of enzyme remained after two-week preservation by 90 degrees F/85%RH (relative humidity). The stability of the enzyme which is not coated with the bottom of the same conditions was 7.4%. Although this can obtain the stability which can be admitted, it shows that it becomes impossible to admit stability if coating is not chosen carefully.

example 3 The polyethylene glycol was used for coating of a hydrolase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the

warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 3g a rate for /by the nozzle to up to the enzyme which mobilized 20% of PEG Carbowax\*\* (Union Carbide) and 30% of water, and the solution of 50% of ethanol. The temperature which was governing the inside of a turbulent flow exhaust air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 20.6% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 0.75 minute, and showed 90% of solubility in 1.5 minutes. The stability in the dperoxyacid bleaching constituent of the coated enzyme was 13.8% of enzyme remains after two-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which was not coated was 7.4%.

This shows that mere physical separation is not enough to protect an enzyme from an oxidizing compound. It works so that an oxidizing compound may be neutralized, and the chemical barrier which gives the suitable fusibility for a detergent bleach is required.

**example 4 Alcalase of four copies (weight)** \*\*2.0T was added at 100 degrees F (37.8 \*\*) to **Neodol of one copy** \*\*45-7 (shell) within the beaker. It added until it became sodium carbonate of eight copies of total amounts, agitating one copy of sodium carbonate at a time violently at a stretch. Weight increase percentage was about 225% to the weight of an enzyme. It under the same conditions of the enzyme which is not coated compared with the stability of the enzyme coated with 100 degrees F four weeks afterward having been 83% in the dry bleaching constituent containing about 20% of peroxy-acid grain was 67%.

**example 5** The sodium silicate of the modulus 2.00 was used for coating of a hydrase enzyme. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 7g a rate for /by the nozzle to up to the enzyme which diluted the "D" sodium silicate to solid content 25%, and mobilized it from 44% solid content with water. The temperature which was governing the inside of a turbulent flow exhaust air mixer was about 50 degrees. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 22.5% of the weight of the uncoated enzyme. In the detergent solution, in 2 minutes, when the granule was for 50% of solubility, and 4.5 minutes, it showed 90% of solubility at 20 \*\*. The stability under the same conditions of the enzyme which the stability of the coated enzyme is 74% of enzyme remains in four weeks, and is not coating it with 90 degrees F/85% relative humidity was 4%.

**example 6** The transition metal was added to the sodium silicate of Example 5.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 6g a rate for /by the nozzle from on the enzyme which mobilized the thing for which "D" sodium silicate solution was made to contain 100 ppm copper (as copper sulfate), iron (as ferrous sulfate), cobalt (as cobalt sulfate), and nickel respectively (as nickel sulfate). The temperature which governed the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme constituent which flows easily was obtained and, subsequently it was coated. The coated enzyme occupied 22% of the weight of the enzyme which is not coated. The granule showed 50% of solubility in 2.5 minutes at 20 \*\* in the detergent solution, and showed 90% of solubility in 5.0 minutes. The stability under the same conditions of the enzyme which 87% of enzyme remained four weeks afterward, and the stability in the inside of the dperoxyacid bleaching constituent of the coated enzyme is not coating with 90 degrees F/85% relative humidity was 4%.

**example 7** Sodium carbonate was added to the sodium silicate of Example 5.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 6g a rate for /by the nozzle to up to the enzyme which mobilized the solution which comprises 15% of "D" sodium silicate solid content, 10% of Na<sub>2</sub>CO<sub>3</sub>, and 75% of water. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme constituent which flows easily was obtained and, subsequently it was coated. The feature of the coated enzyme was as follows. Coating occupied 20.5% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 1.5 minutes, and showed 90% of solubility in 3.5 minutes. As for the stability in the dperoxyacid bleaching constituent of the coated enzyme, 66% of enzyme remained after four-week preservation with 90 degrees F/85% relative humidity. The stability under the same

conditions of the enzyme which is not coated was 4% remains.

example 8 Sodium sulfite (reducing agent) was added to the sodium silicate of Example 5. Alcalase\*\*2.0T of 200 was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (50-55 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . Sodium sulfite was melted in water. Subsequently, this was added to the "D" sodium silicate and it was considered as the solution containing 1.2% of "D" sodium silicate solid content, 8.4% of sodium sulfite, and 79% of water. The spray was carried out at 7g a rate for /by the nozzle to up to the enzyme which mobilized this solution. The temperature which governs the inside of a turbulent flow exhaust air mixer was about 50 \*\*. The granulated enzyme which flows easily was obtained and, subsequently this was coated. The coated enzyme had the following features. Coating occupied 17% of the weight of the uncoated enzyme. Coating was aimed at 60% of "D" sodium silicate and 40% of sodium sulfite being included. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 2 minutes, and showed 90% of solubility in 3 minutes. The stability in the diperoxyacid bleaching constituent of the coated enzyme was 68% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity.

example 9 The sodium silicate of the modulus 3.22 was used for coating of the hydrase enzyme. Solubility fell remarkably compared with the sodium silicate of the modulus 2.0. 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (45-50 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The "N" sodium silicate was diluted from solid content (at the time of purchase) with water to solid content 25% 44%. The spray was carried out at 5g a rate for /by the nozzle to up to the enzyme which mobilized this solution. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 45 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The feature of the coated enzyme was as follows. Coating occupied 35% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 55% of solubility in 11.5 minutes, and showed 90% of solubility in 20 minutes. The stability in the diperoxyacid bleaching constituent of the coated enzyme was 64% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which is not coated was 4%.

example 10 Polyvinyl alcohol was used as coating of a hydrase enzyme. Although solubility was good, the stability after four-week preservation of an enzyme was not able to be admitted. Sodium lauryl sulfate was added for reduction with Neva.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized there by the flow of the warm air (40 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 3g a rate for /by the nozzle to up to the enzyme which mobilized 4.9% of polyvinyl alcohol, 6.1% of sodium lauryl sulfate, 44.5% of water, and the solution of 44.5% of ethanol. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 35-40 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzymes were the following features. Coating occupied 9% of the weight of the uncoated enzyme. In the detergent solution, at 20 \*\*, the granule showed 50% of solubility in 1 minute, and showed 90% of solubility in 2 minutes. The stability in the diperoxyacid bleaching constituent of the coated enzyme showed 3.6% remains of the enzyme after four-week preservation with 90 degrees F/85% relative humidity. The stability under the same conditions of the enzyme which is not coated was 4% remains.

example 11 When BHT (anti-oxidant) was added to polyvinyl alcohol of Example 10, enzyme stability increased remarkably.

200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it \*\*\*\*\*\*(ed) there with the flow of the warm air (40 \*\*) at the time of abbreviation 130m<sup>3</sup>/ . The spray was carried out at 4g a rate for /through the nozzle to up to the enzyme which mobilized 4.44% of polyvinyl alcohol, 5.56% of sodium lauryl sulfate, 0.1% of BHT, 44.5% of water, and the solution containing 44.9% of ethanol. The temperature which governed the inside of a turbulent flow exhaust air mixer was about 35-40 \*\*. The granulated enzyme constituent which flows easily was succeeded to it and coated. The coated enzymes were the following features. Coating occupied 10.5% of the weight of the uncoated enzyme. Coating was aimed at comprising 44% of polyvinyl alcohol, 55% of sodium lauryl sulfate, and 1% of BHT. The stability in the diperoxyacid bleaching constituent of the coated enzyme was 32% of enzyme remains after four-week preservation in 90 degrees F/85% relative humidity. The stability under the same conditions of an uncoated enzyme was 4% remains.

example 12 As another example, the silicate was used for encapsulating an enzyme combining

a transition metal. Subsequently, this capsule was mixed with the dry bleaching constituent which uses sodium percarbonate as a base. In the above-mentioned examples 5-6, similarly, 200-g Alcalase\*\*2.0T was put into the fluid bed spray coater, and it mobilized by the flow of the warm air (50-55 \*\*) at the time of rate-of-flow abbreviation 130m<sup>3</sup>/. Every 100 ppm copper (as CuSO<sub>4</sub>), iron (as FeSO<sub>4</sub>), The spray was carried out at 6g a rate for /through the nozzle to up to the enzyme which mobilized the "D" sodium silicate for which cobalt (as CoSO<sub>4</sub>) and nickel are contained (as NiSO<sub>4</sub>). Subsequently, the letter enzyme mixture of a flow was coated. Coating occupied 22% of the weight of the uncoated enzyme as in Example 6. The enzyme in which the stability of the enzyme in the dry bleach of a percarbonate base remains after four-week preservation with 90 degrees F/85% relative humidity was 89%. A percarbonate constituent 54.6% of Na<sub>2</sub>CO<sub>3</sub>, 43.96% of percarbonate, 0.68% of Tinopal 5 BMX-C (a fluorescence white agent, Ciba-Geigy), 0.48% of charge of aroma, and 0.28% of TritonX-100 (a non-ion system surface-active agent -- anti- -- powdering -- an agent) were comprised. Although the stability (with no transition metal) of the coated enzyme was good, it was \*\*\*\*\* (about 79%) stability per same period. Un-coating Alcalase was poor stability (19%) per same period. About long-term stability, the alcalase coated with both the silicate and the transition metal showed stability with 24 good weeks under the same temperature/relative humidity. That is, it is about 73%. Remains activity was 52% and 58%, respectively about the 24 weeks when the alcalase coated only with the silicate and uncoated alcalase are the same. The stability of Milezyme\*\* was as low as about 2%. This is shown to Fig. 5 by the graph. As mentioned above, although the constituent useful as a domestic bleach was explained, this invention also has intention of change and correction which enter within the limits of it.

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#### **Brief Description of the Drawings**

The scanning electron micrograph in which the particulate structure of the enzyme (Alcalase\*\*2.0T) which Fig. 1 is not coating is shown,  
Fig. 2 -- the sodium silicate of the modulus (ratio of SiO<sub>2</sub>:Na<sub>2</sub>O) 2.00 -- the increase of weight - - the scanning electron micrograph in which the particulate structure of the enzyme (Alcalase\*\*2.0T) coated to 25.5% is shown,  
Fig. 3 -- core carrier material and an enzyme layer -- and -- anti- -- powdering -- the type section figure of an enzyme grain with a film layer,  
Fig. 4 is a type section figure of the grain which covered the enzyme grain as shown in Fig. 3 with protective coating according to this invention,  
Fig. 5 is a graph which shows the comparative stability of the enzyme in an oxidizer (sodium percarbonate).  
Main numerals  
1 .... Core carrier material, 2 .... Enzyme layer  
3 .... A film layer, 4 .... Soluble protective coating

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#### **Fig. 1**

For drawings please refer to the original document.

#### **Fig. 2**

For drawings please refer to the original document.

#### **Fig. 3**

For drawings please refer to the original document.

#### **Fig. 4**

For drawings please refer to the original document.

**Fig. 5**

For drawings please refer to the original document.

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